Thermodynamic / Kinetic Parameters

Thermodynamic:

$$A \underset{}{\overset{K}{\rightleftharpoons}} B$$

forward rate const.: k_1
reverse rate const.: k_{-1}

$$Q = [B] / [A]$$

$$K = Q_{eq} = [B]_{eq} / [A]_{eq}$$

$$\Delta G = RT \ln(Q / K),\ \Delta G° = -RT \ln K$$

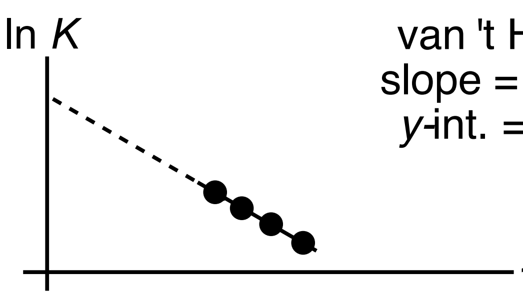
When $Q = 1$, $\Delta G = \Delta G°$
At equilibrium, $Q = K$, so $\Delta G = 0$

When $\Delta G° = 0$, $K = 1$

$$\boxed{K = \exp(-\Delta G° / RT)}$$

Since $\Delta G° = \Delta H° - T\Delta S°$,
$$\ln K = -\Delta G° / RT = -\Delta H° / RT + \Delta S° / R$$

298 K: $\Delta G° = -1.36$ kcal/mol (lg K)



van 't Hoff plot:
slope = $-\Delta H° / R$
y-int. = $\Delta S° / R$

Kinetic:

$$A \xrightarrow{k} B$$

Arrhenius (overall kinetics)

$$\boxed{k = A \exp(-E_a / RT)}$$

Eyring (single step)

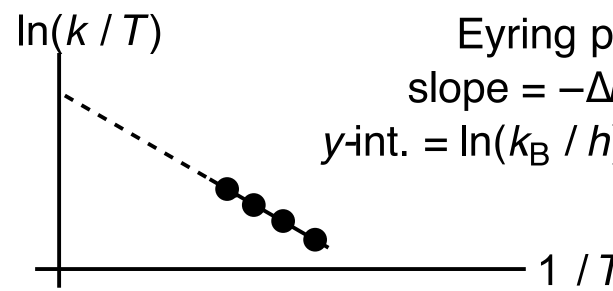
$$\boxed{k = (k_B T / h) \exp(-\Delta G^{\ddagger} / RT)}$$

For a single-step rxn:

$$E_a = \Delta H^{\ddagger} + RT,\ A = (e k_B T / h) \exp(\Delta S^{\ddagger} / R)$$
(e = 2.718...)

Since $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$,
$$\ln(k / T) = \ln(k_B / h) + \Delta S^{\ddagger} / R - \Delta H^{\ddagger} / RT$$

298 K: $\Delta G^{\ddagger} = 23$ kcal/mol $\Rightarrow k = 10^{-4}\ s^{-1}$



Eyring plot:
slope = $-\Delta H^{\ddagger} / R$
y-int. = $\ln(k_B / h) + \Delta S^{\ddagger} / R$

$$K = k_1 / k_{-1} \text{ and } \Delta G° = \Delta G^{\ddagger}_1 - \Delta G^{\ddagger}_{-1}$$